Inorganic Clathrates for Hydrogen Storage

V. V. Struzhkin, W. L. Mao, B. Militzer
H.-k. Mao, R. J. Hemley
Carnegie Institution of Washington

May 23, 2005

DOE 2005 Hydrogen Program Annual Review, Washington, D.C.

This presentation does not contain any proprietary or confidential information.

Project ID
STP48

Overview

Timeline

- Start 04/01/2005
- End 04/01/2009
- 1% complete

Budget

- Total project funding
  - $1,160,351 from DOE
  - $290,088 from CIW
  - No funding received in FY04
- Funding for FY05 : $200,000 from DOE, $74,410 from CIW

Barriers

- Weight and Volume
- Refueling Time
- Hydrogen Capacity and Reversibility
- Lack of Understanding of Hydrogen Physiosorption

Partners/collaboration

- LANL Lansce-12, Yusheng Zhao
- BNL, NSLS, Chi-Chang Kao

Project Objectives

Develop and demonstrate reversible hydrogen storage **CH_4, H_2O - based clathrate** materials with at least 7 wt.% gravimetric and 50 g H_2/L materials-based volumetric capacity, allowing refueling time 1kg H_2/min, with potential to meet DOE 2010 system-level targets.

- H_2-CH_4-X and H_2-H_2O-X Systems. Explore P-T conditions and additional components X (promoters, or guest molecules) that will stabilize the clathrate structure.
- Computer simulation study of binary and ternary systems to understand structural details and stability, molecular dynamics to predict new phases and characterize their stability and structural details
- A dedicated gas loading system will be developed for synthesis and recovery of hydrogen-based molecular compounds. The system will be used at neutron facilities in structural and vibrational dynamics studies, for investigation and optimization of new low-pressure synthesis routes and discharge kinetics.

Approach

- Clathrates with very high H_2 contents were synthesized in diamond anvil cells at high pressure and low temperature; clathrate formation and hydrogen release are spontaneous.
- Challenge: extend the P-T stability field to near ambient P and T.
- Approach: stabilize clathrates with additional guest molecules (promoters)

➢ Testing at least 5 promoters for each of two systems (H_2O, CH_4) and achieve reproducible measurement of storage capacity

➢ Selection of optimum material: demonstration of material with reversible capacity > 3 wt.% by the end of the first year

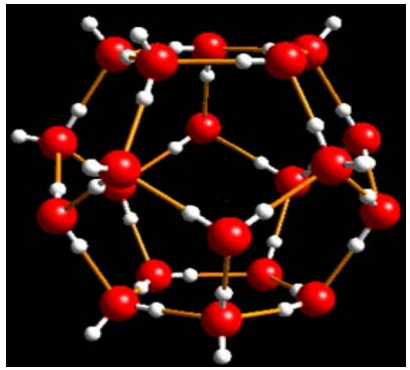
➢ Selection of two compositions viable for a reversible capacity of greater than 5 wt.% and temperature of the dry ice -78 C

➢ Optimization of hydrogen storage material to reach materials-based gravimetric capacity 6 wt%, materials-based volumetric capacity 40 g H2/L, and allowing refueling time 0.5 kg H2/min

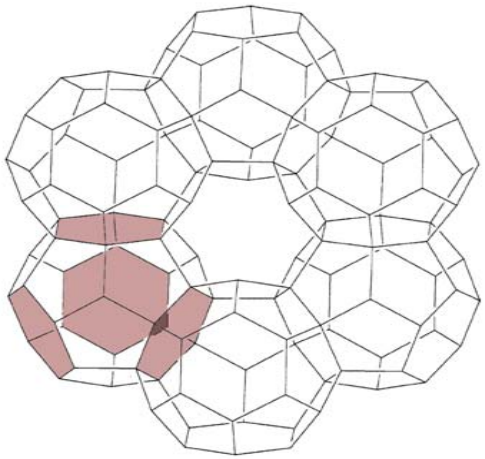
➢ Further optimization to achieve materials-based gravimetric capacity 7 wt% , materials-based volumetric capacity 50 g H2/L, and allowing refueling rate of 1 kg H2/min

Clathrates: Properties

Building clathrate cages from hydrogen-bonded water molecules

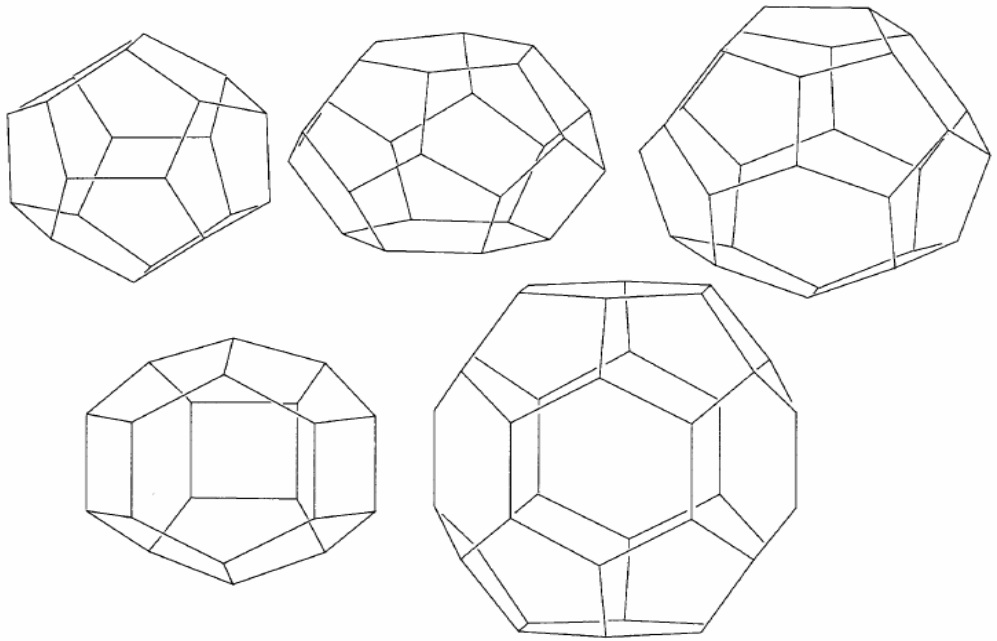


Structure II

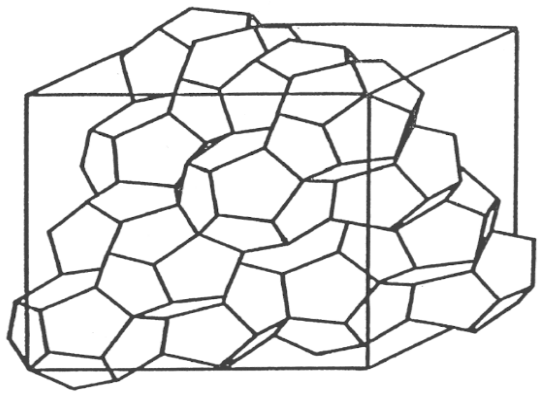


Large cages (16-hedra) in tetrahedral symmetry

12-hedra: 5^{12} 12-hedra: $5^{10}6^2$ 16-hedra: $5^{12}6^4$



12-hedra: $4^3 5^6 6^3$ 20-hedra: $5^{12}6^8$

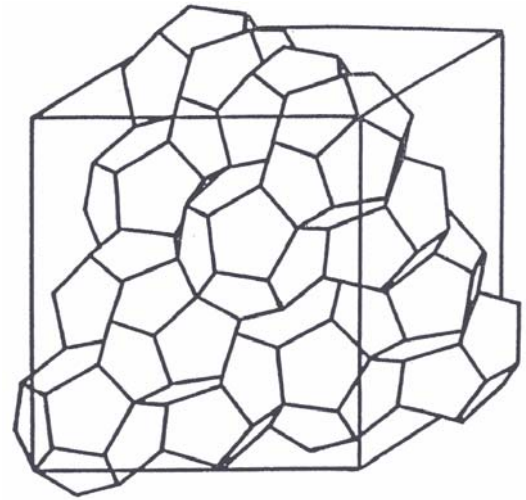


Diamond-like structure

M.T.Kichner, R. Bose, W.E.Billups, L.R.Norman, J. Am. Chem Soc. 126 (2004) 9407-9412.

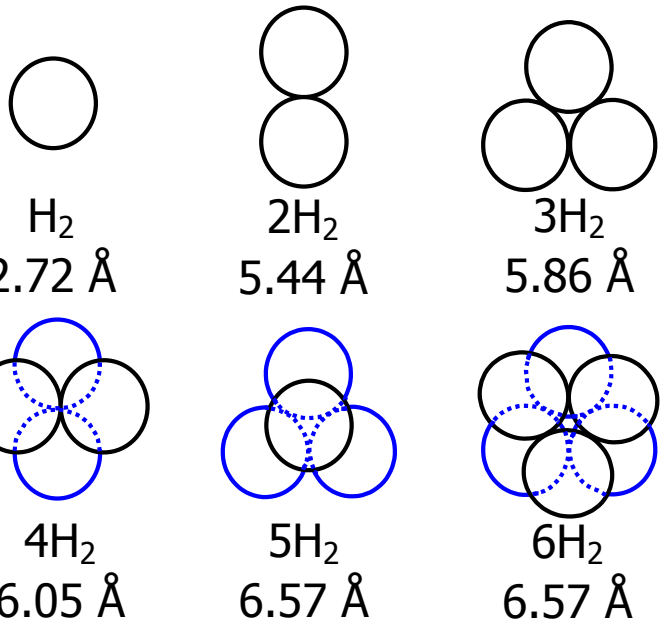
Clathrates: properties

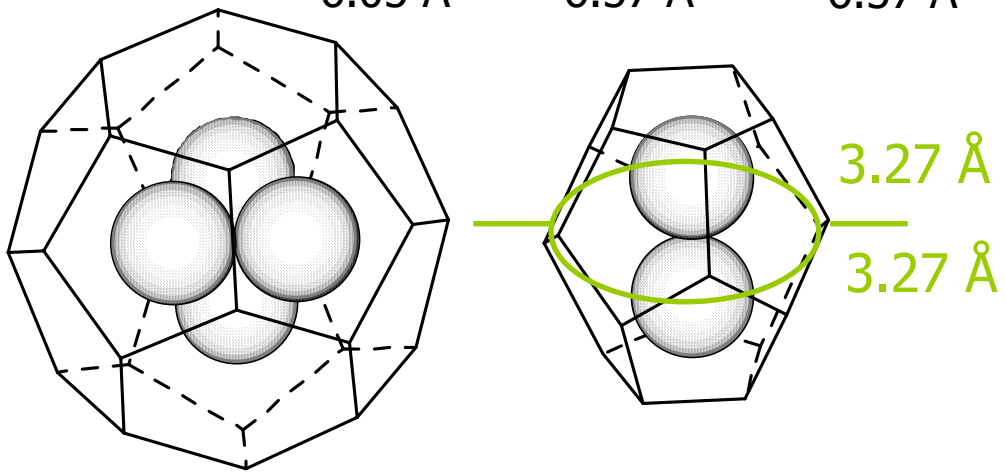
Structure II is stabilized at moderate P,T –conditions; it accepts H_2 molecules in large ($4xH_2$) and small ($2xH_2$) cages



- structure II
- $64H_2:136H_2O$
- 4 * 8 + 2 * 16 = 64
- 6 * 8 + 1 * 16 = 64

Small cage Large cage





$5^{12}6^4$
8 cages
6.67 Å

5^{12}
16 cages
5.02 Å

Technical Approach

- H_2-H_2O system
- H_2-H_2O-X systems, select X from different materials cathegories that form clathrates (H_2O-X)
  - Argon (very small, double occupation, space for H_2)
  - Organic molecules e.g. trimethylamine $4(CH_3)_3N$-$41H_2O$
  - (guest location fixed, nitrogen distort the cage structure slightly)
  - Strong acid e.g. HBF_6 or $HClO_4$ (anionic guest)
  - Tetrahydrofuran (THF)
  - Strong cages, i. e. $(LiOH)_x(H_2O)_{1-x}$
- H_2-X-CH_4 system, X is selected to optimize clathrate structure, X could be a mixture of water and all of the above

Goal: Stabilize clathrate at near ambient T and P

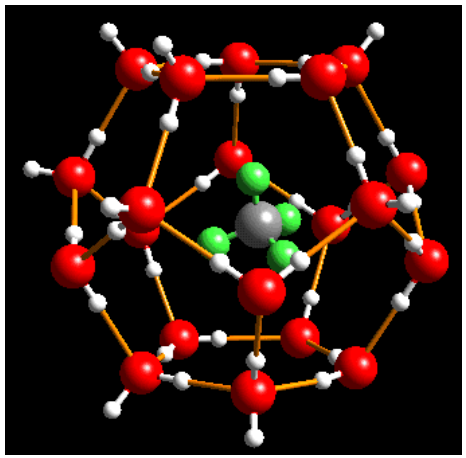
Maximize H_2 capacity

Theoretical Approach

Theoretical Descriptions Relies on a Three-prong approach

Computational methods order with increasing accuracy:

1. Classical simulation: molecular dynamics with 1000s of atoms



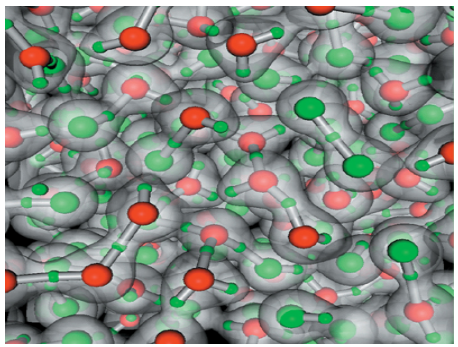
- Molecular dynamics using predefined force-fields:

$$F = m\,a$$

- Very fast → Simulations of many cages possible
- However, the accuracy depends on force fields that contain all information about chemical bonds and interactions.
- Study the cage stability with increasing T → melting.
- Combine results with free energy calculations.

- Introduce different guest molecules
- Use simulation to select promising guest candidates

2. Ab initio level description: structure relaxations in unit cell



Ab initio simulation (Gygi, Livermore)

- Electrons are quantum mechanical (wavefunctions Ψ).
- Schroedinger equation solved (density function theory)

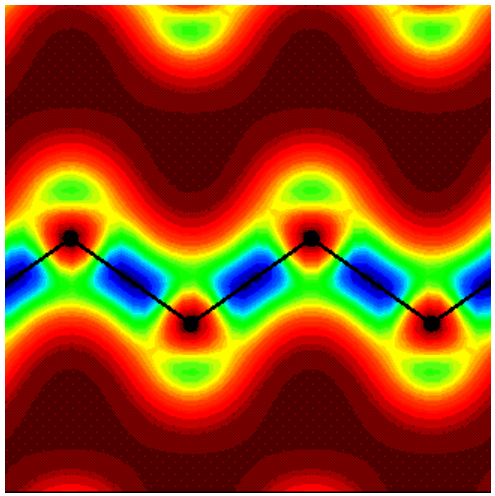
$$\hat{H}\ \Psi = E\ \Psi$$

- Ions are classical: F = m a
- Accurate host-guest interaction → cage deformation
- Disorder
- Electronic and vibrational properties
- Orientation of guest molecules e.g. off-center location
- High pressure properties

Theoretical Approach

3. Quantum Monte Carlo calculation: static calculations

In quantum Monte Carlo, one propagates a correlated ensemble of walkers in order to project out the groundstate wavefunction.



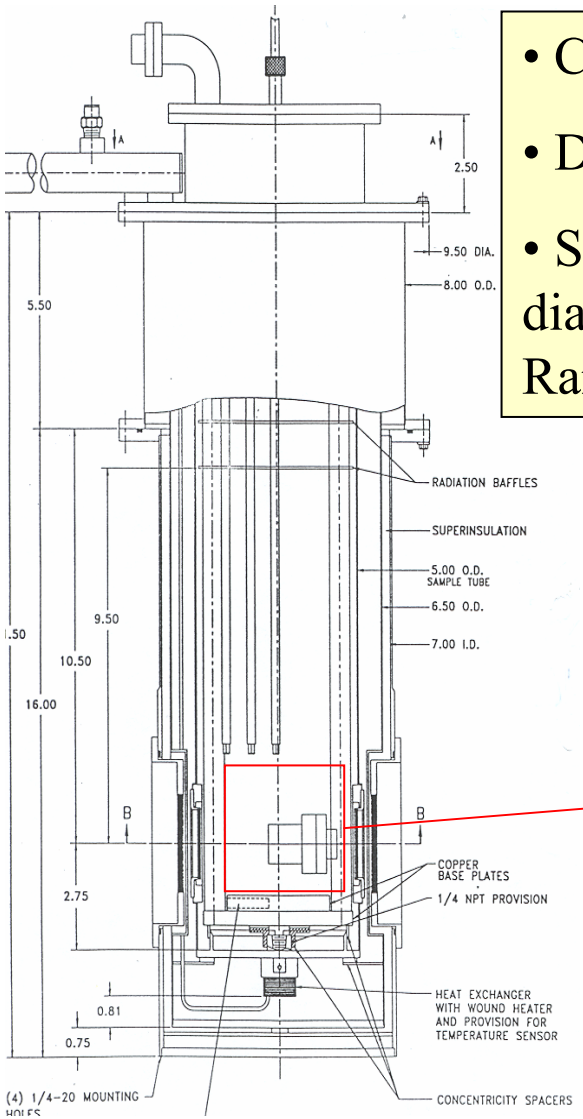
QMC study of exchange-correlation effects in bulk silicon (Foulkes).

Advantages:
- Electronic correlation effects are included.
- Van der Waal interactions can be described.
- Study of H_2 - water cage interaction
- Study of precise arrangements of molecules in cage
- Study of multiple H_2 accupancy effects

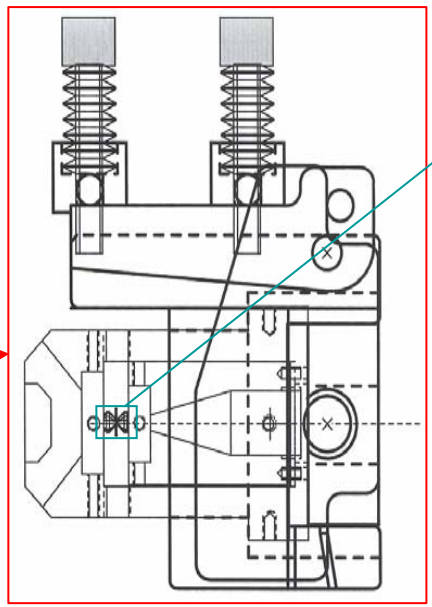
Disadvantages:
- Method is very expensive
- Dynamics is currently not feasible

Technical Approach

Spectroscopy:Experimental Set-Up

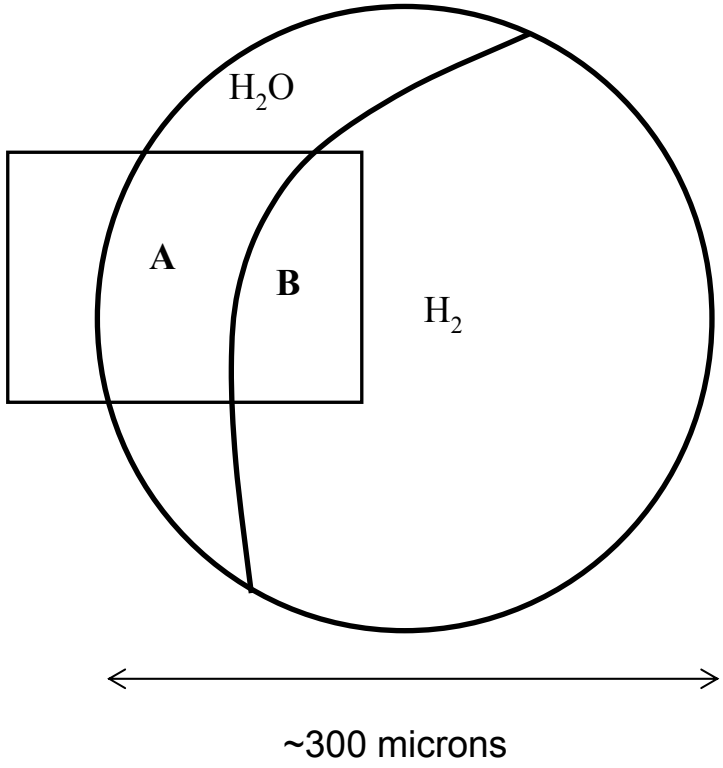


- Cryostat 4 K-320 K
- Diamond anvil cell
- Selection of high quality diamonds for IR and Raman experiments



Accomplishments

Clathrate formation in a diamond anvil cell



Hydrogen content : ~0.45
5.265 wt % molecular hydrogen

Mao *et al*, Science 2002

300 MPa
250 K

249 K
t = 0

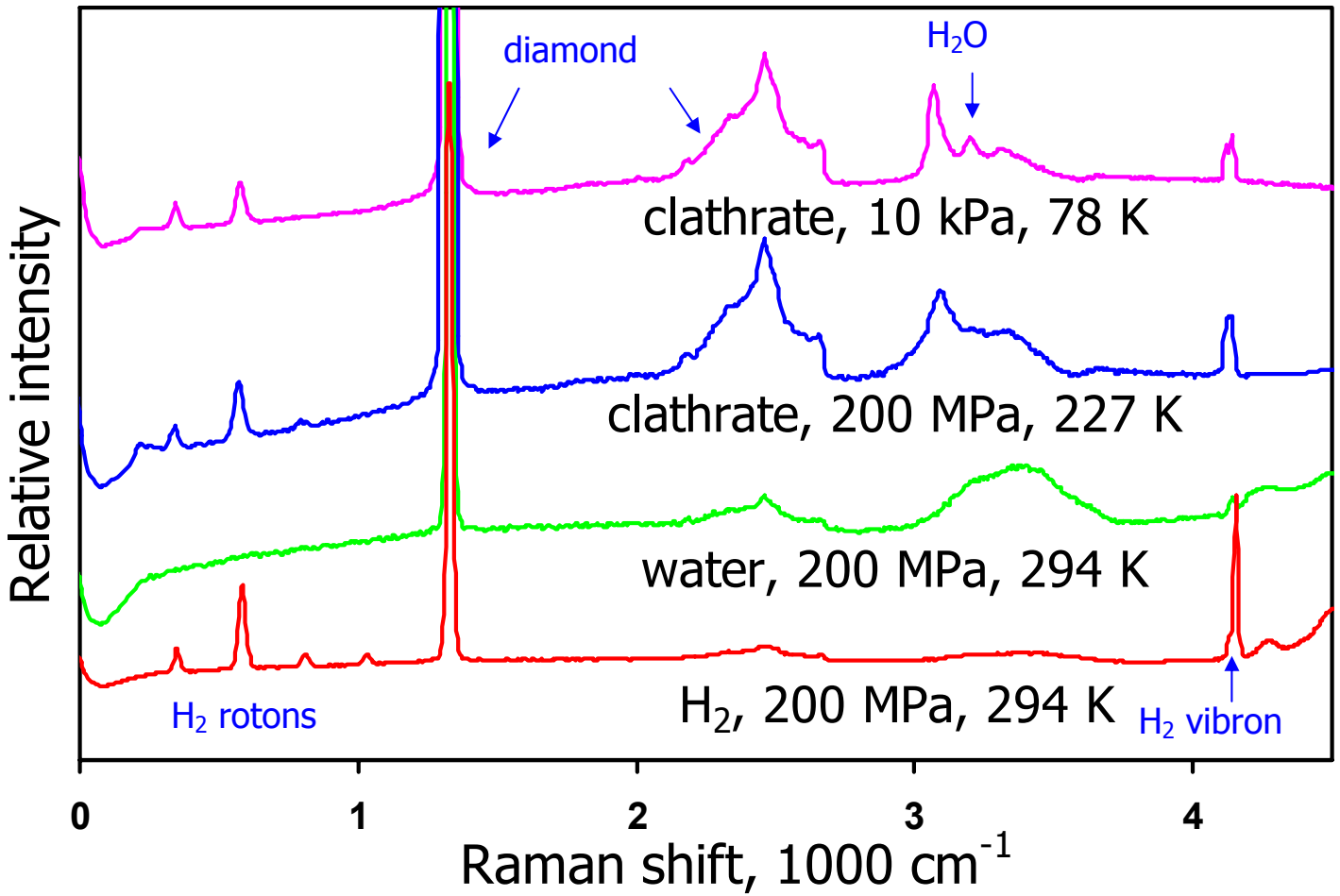
t = 30 min

Clathrate formation at 249 K: sluggish kinetics

Accomplishments

Raman Spectroscopy

Mao *et al*, Science 2002

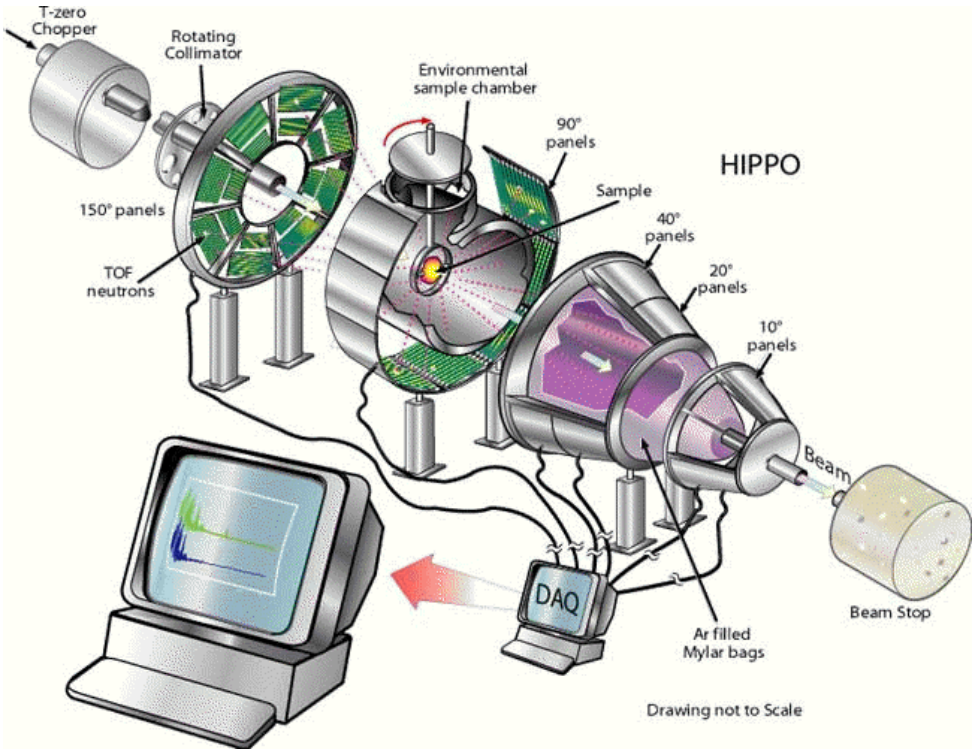


Raman spectroscopy gives information on hydrogen vibron frequency, which provides a measure of physiosorption strength, and also of hydrogen molecule's freedom to rotate (roton region below 600 cm^{-1}). H_2O stretching bands allow to extract the information on clathrate structure and to provide a reference for quantitative determination of hydrogen content in a clathrate.

Accomplishments

Neutron scattering

Lokshin *et al*, PRL 2004.

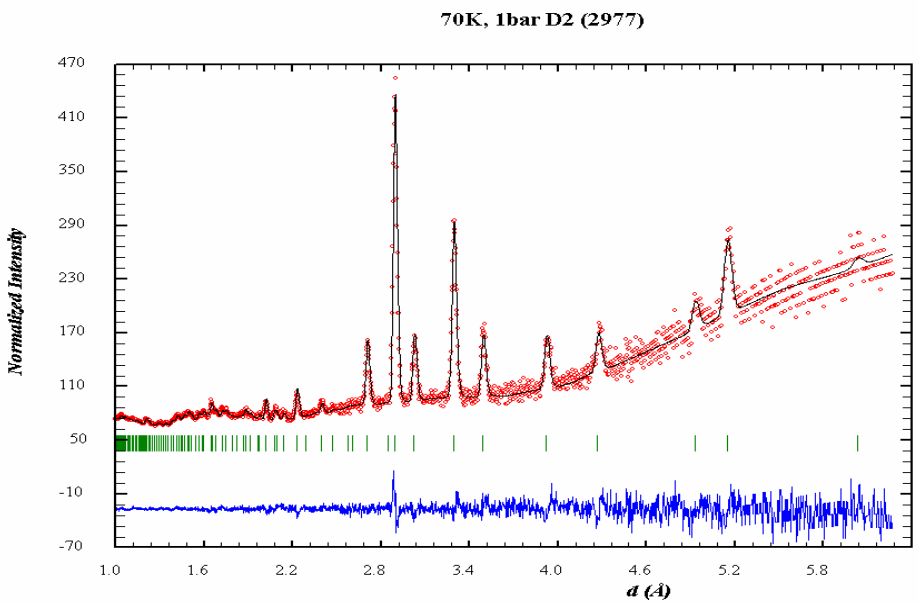


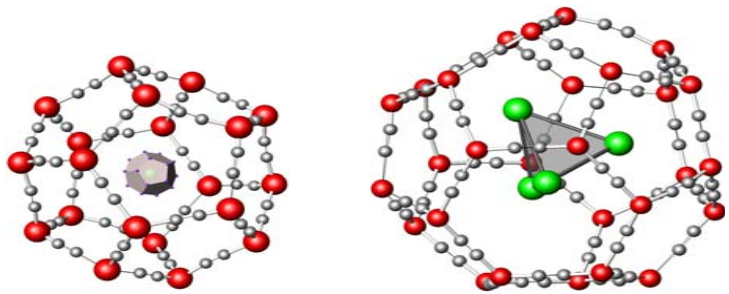
- Aluminum cell
- Half-filled cell with D_2O
- Pumped D_2 into remaining volume to almost 0.2 GPa

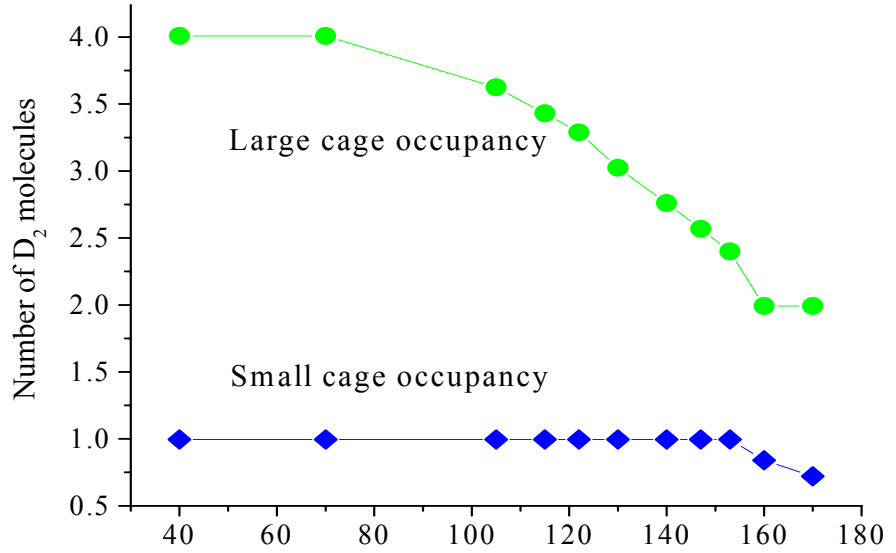
The D_2 clathrate hydrate crystal structure was determined as a function of temperature and pressure by neutron diffraction for the first time. The hydrogen occupancy in the $(32+X)H_2 \cdot 136H_2O$, x=0-16 clathrate can be reversibly varied by changing the large (hexakaidecahedral) cage occupancy between two and four molecules, while remaining single occupancy of the small (dodecahedral) cage. Above 130–160 K, the guest D_2 molecules were found in the delocalized state, rotating around the centers of the cages. Decrease of temperature results in rotation freezing followed by a complete localization below 50 K.

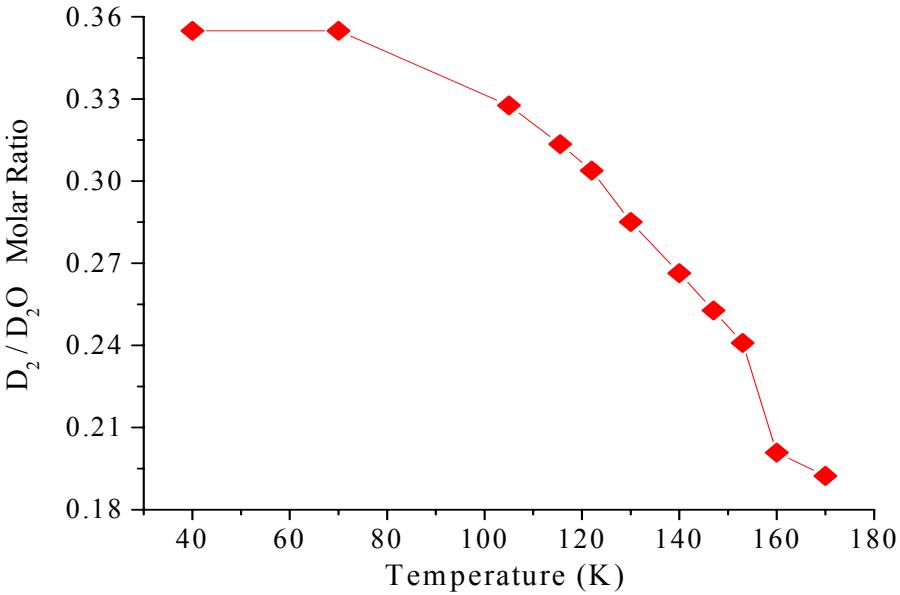
Accomplishments

Neutron study of cage occupancy









Lokshin *et al*, PRL 2004.

Accomplishments

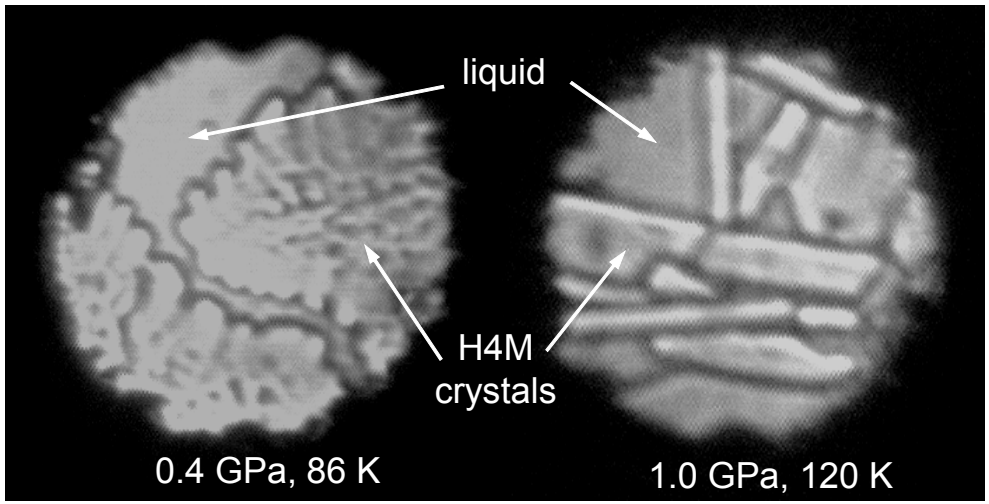
H_2-H_2O Molecular Ratio (R) from different techniques discussed in previous slides

- Volume estimate in DAC
  - R=0.45 (±0.05) (approximately 5.27 wt %)
- Raman intensity of H_2 (vibron and roton)
  - R=0.48 (±0.04)
- Neutron study
  - R=0.33

Accomplishments/Progress

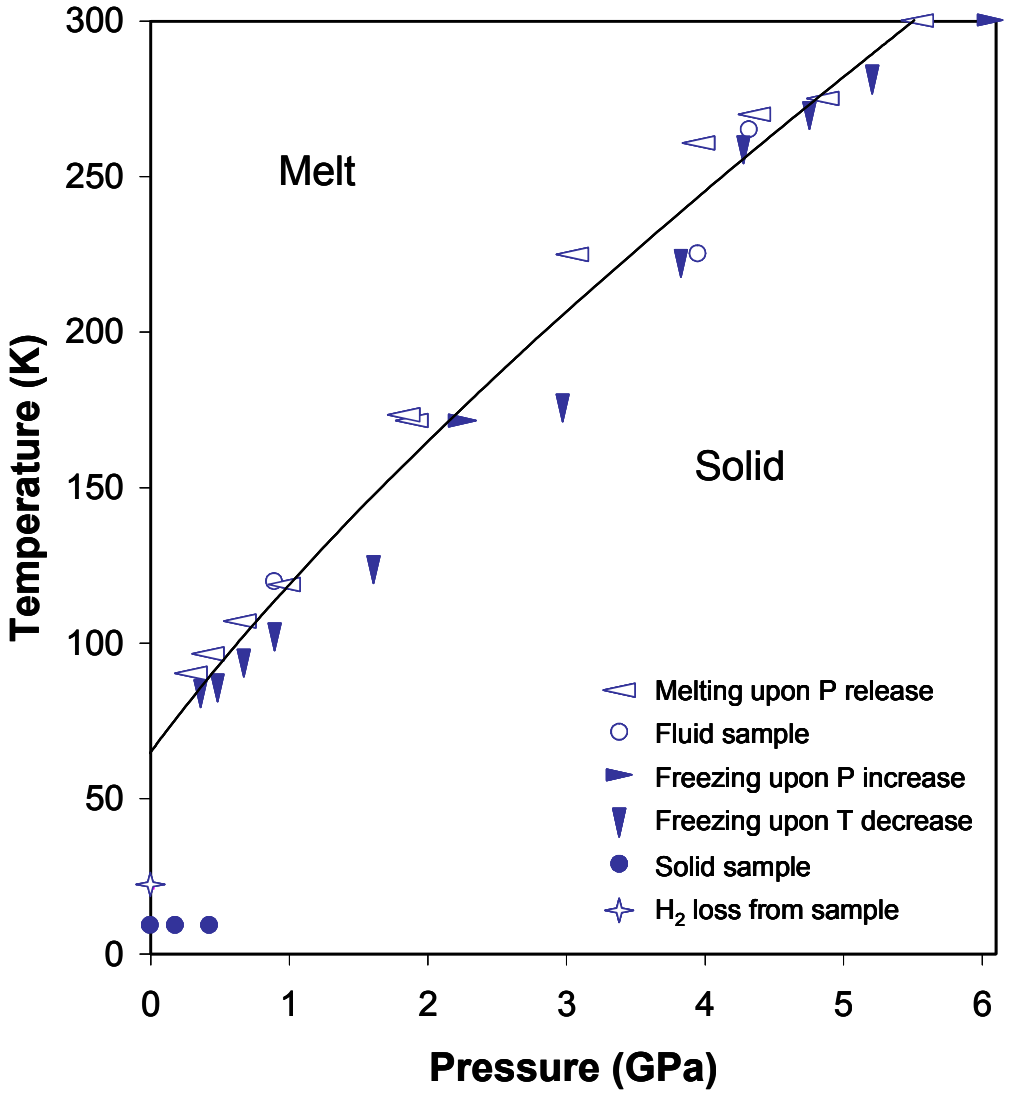
Melting of $[H_2]_4CH_4$ (called H4M below)

Photomicrographs showing crystals of H4M growing from the fluid for different *P-T* conditions.



Accomplishments/Progress

H4M melting curve

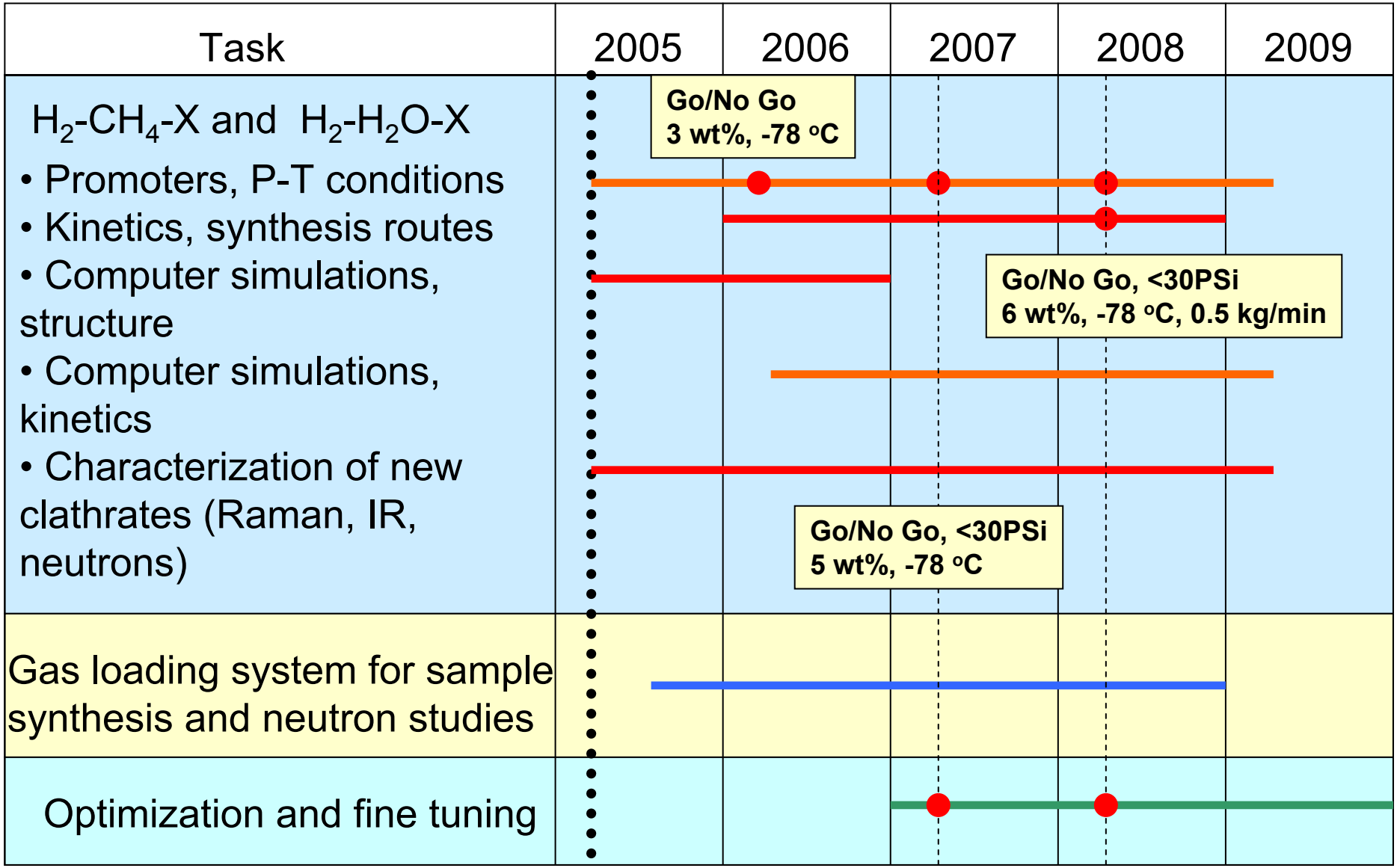


Melting curve of $(H_2)_4CH_4$. Melt refers to a fluid mixture of H_2 and CH_4. This material demonstrates the potential of hydrogen plus simple hydrocarbon systems, and opens the vast area of searching for novel hydrogen-rich compounds with other alkanes and hydrocarbons. We also propose to add other components to stabilize $(H_2)_4CH_4$ to higher T

Future Work

Year 2005:
Task 1: H2-CH4-X and H2-H2O-X Systems. Explore P-T conditions and additional components X (promoters) that will stabilize the large-cage clathrate structure.
Task 2: Computer simulation study of binary and ternary systems to understand structural details and stability
Task 3: A dedicated gas loading system will be developed for synthesis and recovery of hydrogen-based molecular compounds. The system will be used at neutron facilities in structural and vibrational dynamics studies.
Year 2006:
Task 4: Further studies of H2-CH4-X, H2-H2O-X systems, down-selection of two most promising compositions.
Task 5: Characterization of the optimized clathrate phases by Raman, IR, x-ray diffraction, and neutron diffraction.
Task 6: Investigation and optimization of new low-pressure synthesis routes and discharge kinetics.
Task 7: Computer simulation study of optimized ternary systems including molecular dynamics to predict new phases and characterize their stability and structural details.
Task 8: A dedicated gas loading system will be modified and extended to allow measurements of the kinetics/thermodynamics of release and storage and measurements of gravimetric and volumetric capacity of new materials.

Project Timeline



Publications and Presentations

H.-k. Mao, W. L Mao, V. V. Struzhkin, Hydrogen Storage in Molecular Compounds, presented at ASM Int. Conf, Columbus, OH, October 18-21, 2004.

W. L. Mao, V. V. Struzhkin, H-k. Mao, and R. J. Hemley, P-T stability of the van der Waals compound $(H_2)_4CH_4$, Chem. Phys. Lett. 402, 66-70, 2005.

K. Lokshin, Y. Zhao, D. He, W. L. Mao, H-k. Mao, R. J. Hemley, M. V. Lobanov, and M. Greenblatt, Structure and dynamics of hydrogen molecules in the novel clathrate hydrate by high pressure neutron diffraction, Phys. Rev.Lett., 93, 125503, 2004.

W. L. Mao and H-k. Mao, Hydrogen storage in molecular compounds, PNAS 101, 708-710, 2004.

W. L. Mao, “Hydrogen storage in molecular compounds,” 2004 SSAAP Symposium, Albuquerque, NM, March 2004 (poster).

W. L. Mao, “Hydrogen storage in molecular compounds,” 2003 LANSCE User Group Meeting, Los Alamos Neutron Science Center, Los Alamos, NM, October 2003 (invited talk).

W. L. Mao, “Neutron study of hydrogen clathrate,” 2003 COMPRES Meeting, Santa Cruz, CA, June 2003 (poster).

W. L. Mao, H-k. Mao, A. F. Goncharov, V. V. Struzhkin, Q. Guo, J. Hu, J. Shu, R. J. Hemley, M Somayazulu, and Y. Zhao, Hydrogen clusters in clathrate hydrate, Science 297, 2247-2249, 2002.